Magnetocrystalline anisotropy and magnetostriction of H and N modified R_2Fe_{17} compounds (R = Y, Tb, Dy, Ho, Er)

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Abstract

The effects of the hydrogen and the nitrogen on the magnetocrystalline anisotropy (MCA) and magnetostriction of $R_2Fe_{17}M$ (R = Y, Tb, Dy, Ho, Er; M = H, N) compounds are studied. The signs of the first MCA constants of a rare-earth (R) sublattice are in agreement with the sign of the Stevens factors of R ions for all $R_2Fe_{17}M$ compounds studied. The effects of the nitrogen and the hydrogen atoms on rare-earth sublattice anisotropy have been found to be opposite. Both hydrogenation and nitrogenation lead to the reduction and change in the signs of the magnetostriction. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The insertion of light interstitial elements (hydrogen, nitrogen, carbon) in the R_2Fe_{17} (R–rare-earth metal) intermetallic compound's (IMC) crystalline lattice results in an apparent change of their magnetic properties (the Curie temperatures, saturation magnetization and magnetic anisotropy) [1–4]. However, the researches on the effect of the insertion elements on the magnetic anisotropy and, especially, magnetostriction of R_2Fe_{17} compounds containing various R-ions are insufficient. Both magnetic anisotropy and magnetostriction of hydrides and nitrides should depend essentially on the

4f-subshell electron structure of individual R-ions. The data on the behavior of the magnetostriction of R_2Fe_{17} nitrides for R–Y, Nd, and Pr reported in Ref. [5] show that the values of anisotropic magnetostriction of these compounds remain relatively low ($< 10^{-4}$) and weakly depend on the temperature in the range of 80–300 K. The purpose of the work is to study the effect of interstitial H and N on magnetocrystalline anisotropy (MCA) and magnetostriction of the R_2Fe_{17} (R = Y, Tb, Dy, Ho, and Er) compounds at different concentrations of interstitial elements.

2. Experimental details

The starting alloys were produced by arc melting appropriate amounts of Fe (99.9%) and R (99.5%)

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in an argon atmosphere followed by heat treatment at 1150°C for 24 h.

The method of hydride and nitride synthesis was described in Refs. [6,7]. The concentration of absorbed hydrogen and nitrogen in the samples was calculated using the van-der Waals equation and additionally was measured by the full burning method. The X-ray diffraction analysis showed that all compounds studied were single-phase and had crystalline structures of Th_2Ni_{17} type.

The magnetic measurements were made for aligned and free powder samples in the temperature range of 80–300 K and in magnetic fields up to 1.2 T using a pendulum magnetometer. Since the majority of the investigated compounds had easy plane anisotropy, the technique of magnetic alignment in a rotating magnetic field [8] was used. The magnetization curves measured on samples oriented along the c-axis and in the basal plane at various temperatures were used to determine the anisotropy constants and its temperature dependence. The magnetization data were corrected for demagnetization assuming a spherical demagnetization factor $D = \frac{1}{3}$ for the dilute mixture of powder in an epoxy resin. The effective anisotropy constant R_1 was calculated [6] from the slopes of the linear part of the hard magnetization curves and from the values of the saturation magnetization determined from the easy magnetization curves. The slope of the curve along the hard direction was determined for an interval of fields from 0.6 up to 1.2 T. For some samples the magnetic measurements were made in pulsed fields up to 15 T at $T = 80$ K [7]. The anisotropy constants determined from the high-field magnetization curves are in a good agreement with those determined from the low-field magnetization curves. A combination of experimental errors in determining R_1 was estimated for some compounds to be about 20% because of the sensitivity of the calculated anisotropy constant to the degree of texture [9]. Unfortunately, hydrides of Tb_2Fe_{17} could be oriented neither in a rotating, nor in a static magnetic field, which could be explained by the cone magnetic structure of the compound at room temperature.

Magnetostriction of R_2Fe_{17} was measured in fields up to 1.3 T in the temperature range of 80K–300 K by using a conventional strain gauge bridge. Since nitrides and some hydrides were available only in powdered form, the measurements were made with powder-pressed samples for all compounds including precursor alloys. This method was successfully applied earlier by Clark et al. [5] for the investigation of the effect of nitrogenation on the magnetostriction of Y_2Fe_{17}, Pr_2Fe_{17} and Nd_2Fe_{17} compounds. The fine powder of R_2Fe_{17} (R = Y, Tb, Dy, Ho, and Er) compounds was mixed with a small amount of cellulose and was compacted under pressure near 1 GPa in to disks with the dimensions of 0.8 mm × 1.5 mm × 8 mm. The densities of the samples produced in this way were nearly 70% of the powder X-ray densities. We took as the magnetostriction value for the investigated compounds, the values measured on the pressed sample multiplied by the ratio of the powder X-ray density to the pressed sample density. This method was checked on a solidified precursor and on hydrogenated samples. The magnetostriction values thus obtained reproduce well for the investigated samples with the same composition, but with different densities of pressed samples. While the effects of bonding with cellulose is a subject of separate investigation and will be reported elsewhere, the most general features of the magnetostriction are reported here. Magnetostrictive measurements were made as a function of magnetic field strength. The absolute error of the magnetostriction measurements was 5×10^{-6}.

3. Results and discussion

R_2Fe_{17} compounds were found to be crystallized in the hexagonal Th_2Ni_{17}-type structure. The single phase was identified for all the samples prepared. Lattice constants a and c, unit cell volume V are listed in Table 1. It was observed that hydrogenation and nitrogenation lead to a lattice expansion of the compounds without a change in the hexagonal symmetry of the parent compounds. The relative cell volume $\Delta V/V$ increases as shown in Table 1. The increase in the unit cell volume is 1.5–6% after hydrogenation and 5–7.6% after nitrogenation.

Table 1
Crystallographic data of the R_2Fe_{17} compounds and hydrides and nitrides

Compound	$a(\text{Å})$	$c(\text{Å})$	c/a	$V(\text{Å}^3)$	$\Delta V/V(\%)$
Y_2Fe_{17}	8.50	8.30	0.98	519	–
$Y_2Fe_{17}H_{3.5}$	8.56	8.31	0.97	527	1.54
$Y_2Fe_{17}H_5$	8.58	8.42	0.98	536	3.28
$Y_2Fe_{17}N_{3.2}$	8.62	8.46	0.98	544	4.82
Tb_2Fe_{17}	8.51	8.31	0.98	521	–
$Tb_2Fe_{17}H_{2.5}$	8.60	8.32	0.97	532	2.11
$Tb_2Fe_{17}H_5$	8.69	8.46	0.97	553	6.14
$Tb_2Fe_{17}N_2$	8.73	8.51	0.97	561	7.67
Dy_2Fe_{17}	8.46	8.30	0.98	514	–
$Dy_2Fe_{17}H_{3.5}$	8.57	8.35	0.97	531	3.30
$Dy_2Fe_{17}H_5$	8.62	8.42	0.98	541	5.25
$Dy_2Fe_{17}N_2$	8.66	8.49	0.98	551	7.20
Ho_2Fe_{17}	8.44	8.31	0.98	512	–
$Ho_2Fe_{17}H_2$	8.54	8.36	0.98	528	3.13
$Ho_2Fe_{17}H_5$	8.60	8.40	0.98	538	5.08
$Ho_2Fe_{17}N_2$	8.61	8.48	1.00	544	6.25
Er_2Fe_{17}	8.44	8.25	1.00	508	–
$Er_2Fe_{17}H_2$	8.50	8.27	1.00	517	1.77
$Er_2Fe_{17}N_2$	8.61	8.43	1.00	541	6.50

Fig. 1. Dependence of the effective anisotropy constant R_1^{Fe} versus the reduced temperature for $Y_2Fe_{17}(N, H)_x$ compounds.

3.1. Magnetocrystalline anisotropy

MCA of a 3d-sublattice was studied for the compounds Y_2Fe_{17}, $Y_2Fe_{17}H_{3.5}$, $Y_2Fe_{17}H_{5.5}$, and $Y_2Fe_{17}N_{3.2}$. Dependencies of the effective anisotropy constants R_1^{Fe} versus the reduced temperature T/T_c are shown in Fig. 1. The variation of the anisotropy constants versus T/T_C is linear in the intermediate temperature range. R_1^{Fe} decreases monotonically with increasing temperature. A comparison of the data for the compounds Y_2Fe_{17} and $Y_2Fe_{17}H_{3.5}$ shows that the addition of 3.5 hydrogen atoms practically does not change MCA of the 3d-sublattice. At the same time it is evident that R_1^{Fe} for the hydrides ($Y_2Fe_{17}H_{5.5}$) and the nitride ($Y_2Fe_{17}N_{3.2}$) are smaller in absolute value than the R_1^{Fe} of the initial compounds. As follows from literature [2], the hydrogen in the $Y_2Fe_{17}H_x$ first occupies octahedral positions and then tetrahedral ones. Therefore, it is supposed that the hydrogen at the octahedral positions do not influence the MCA of the 3d-sublattice in R_2Fe_{17}. The apparent MCA change occurs when hydrogen sits at tetrahedral positions (compound $Y_2Fe_{17}H_{5.5}$), and also when nitrogen enters the
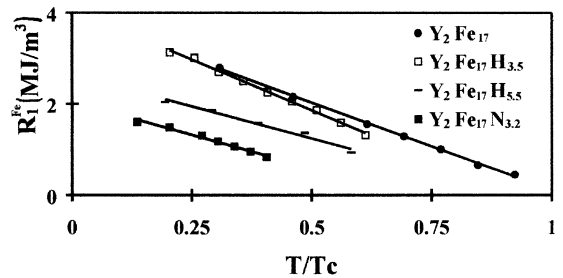
tetrahedral positions ($Y_2Fe_{17}N_{3.2}$ compound). Our results for Y_2Fe_{17} and $Y_2Fe_{17}N_{3.2}$ agree well with data obtained earlier [8].

The effect of hydrogenation and nitrogenation on MCA of the 4f-sublattice was investigated by studying R_2Fe_{17} where R = Tb, Dy, Ho and Er. The values R_1^{Fe} (the Fe contribution of MCA) were taken from the data of Y_2Fe_{17} hydrides and nitrides. The values R_1^R (the 4f-sublattice contribution of MCA) were calculated by subtracting R_1^{Fe} from the experimental R_1 values of the appropriate R_2Fe_{17} hydrides and nitrides. The temperature dependencies R_1^R for Dy_2Fe_{17} and $Dy_2Fe_{17}N_2$, Tb_2Fe_{17} and $Tb_2Fe_{17}N_2$ are presented in Fig. 2. As shown in Fig. 2, R_1^{Dy} and R_1^{Tb} increase in value under nitrogenation, becoming positive for $Dy_2Fe_{17}N_2$ and $Tb_2Fe_{17}N_2$. The values of R_1^R decrease with increasing temperature for all investigated compounds (expect $Dy_2Fe_{17}N_2$). The data for Ho_2Fe_{17}, $Ho_2Fe_{17}H_2$, $Ho_2Fe_{17}H_5$, $Ho_2Fe_{17}N_2$ were obtained earlier [7]. From our experimental results it is concluded that the 4f-sublattice contributions to the total magnetic anisotropy constants R_1^R change its sign due to the hydrogenation and nitrogenation. The effect on R_1^R for hydrides is higher for a concentration of $x = 2$, than for $x = 5$. In the latter case both octahedral and tetrahedral positions are occupied, but the maximum MCA change is observed in the $R_2Fe_{17}H$ compounds where the hydrogen sits at the tetrahedral positions [8].

The R_1^R constants at the hydrogenation and the nitrogenation were obtained for all R_2Fe_{17} compounds. Table 2 generalizes the results obtained. It is evident from Table 2 that the changes in the sign
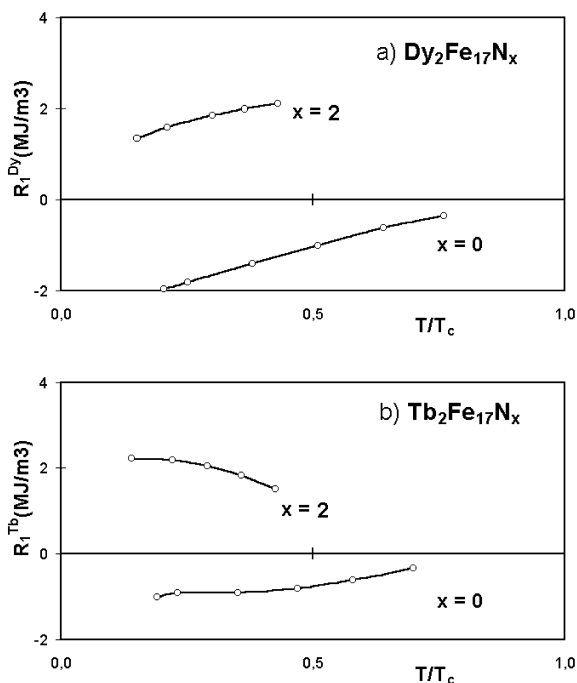
Fig. 2. The rare earth part of R_1^R versus reduced temperature for (a) Dy_2Fe_{17} and $Dy_2Fe_{17}N_2$; (b) Tb_2Fe_{17} and $Tb_2Fe_{17}N_2$.

Using the theory of magnetocrystalline anisotropy of 3d–4f intermetallics [12,13] the crystalline field parameters A_{20} was calculated from $R_1^R(T)$. Our calculations of the change of parameter A_{20} under nitrogenation and hydrogenation give values of $25 \, Ka_o^{-2}$ per hydrogen atom for $Ho_2Fe_{17}H_2$ and $-60 \, Ka_o^{-2}$ per nitrogen atom for $Ho_2Fe_{17}N_2$ [7]. A_{20} can be split into two terms: the contribution from the charges on other atoms in the lattice A_{20} (lat) and the contribution from the charges of the valence electron of the rare-earth atoms themselves A_{20} (val). To explain the difference in influence of the H and N on A_{20} it is necessary to take into account the contribution involved in the interaction of the 4f-subshell with the external valence shell of the rare earth itself which may be deformed by the interstitial atoms [14]. As shown earlier [7], only 'the lattice contribution' cannot satisfactorily explain the behavior of the A_{20} in R_2Fe_{17} after hydrogenation and nitrogenation. The amount of the electrostatic field affecting the 4f-subshell depends not only on the value of ambient atom charges, but probably on the redistribution of electron states in valence shells of R ions as well.

3.2. Magnetostriction

The temperature dependencies of the longitudinal ($\lambda_\parallel$) and transverse ($\lambda_\perp$) magnetostriction differences for the compounds with Tb and Dy are presented in Fig. 3 at 1.3 T. It is seen that hydrogenation and nitrogenation result in the change of ($\lambda_\parallel - \lambda_\perp$) signs (Table 3). For Tb_2Fe_{17} the ($\lambda_\parallel - \lambda_\perp$) value at 78 K is comparatively large and has a positive sign (250×10^{-6}), in $Tb_2Fe_{17}N_2$, however, it decreases in absolute value about five times and has a negative sign. The values of ($\lambda_\parallel - \lambda_\perp$) for $Tb_2Fe_{17}N_x$ and $Dy_2Fe_{17}(H, N)_x$ decrease monotonically with increasing temperature. Low values of magnetostriction and unusual temperature behavior (the maximum ($\lambda_\parallel - \lambda_\perp$) at $T = 180$ K) are observed in $Tb_2Fe_{17}H_{2.5}$ and $Tb_2Fe_{17}H_5$. In $Dy_2Fe_{17}N_2$, the difference ($\lambda_\parallel - \lambda_\perp$) is about 4 times greater in absolute value than in Dy_2Fe_{17}, but has an opposite sign compared to the initial compound. The sign of the transverse and
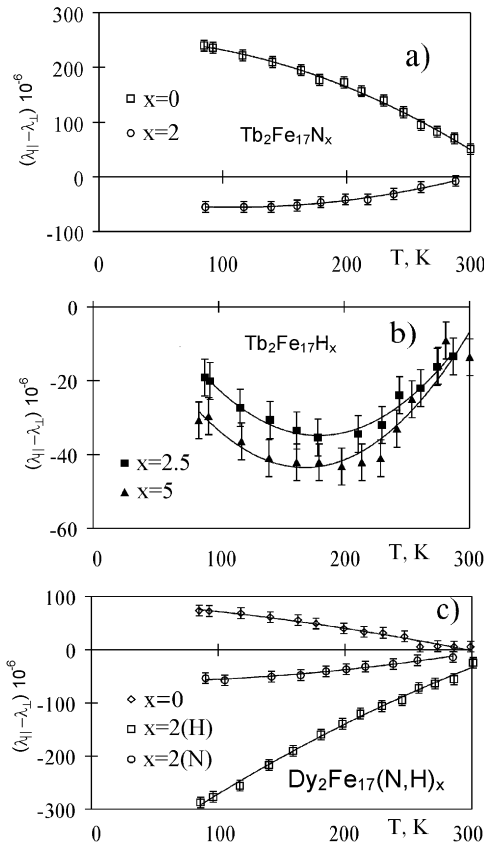
of the anisotropy constants R_1^R after hydrogenation or nitrogenation is in agreement with the signs of α_j, the Stevens factor for R-elements in the R_2Fe_{17} structure. Hydrogenation and nitrogenation cause an opposite change in signs of the anisotropy constants R_1^R.

From this experimental fact we conclude that the main contribution to the magnetic anisotropy in H and N modified R_2Fe_{17} compounds is the crystal field-induced single ion anisotropy on the magnetic rare-earth atoms [10]. In the first approximation the electrostatic interaction of interstitial atoms with R-ions can be considered to depend on the orientation of an anisotropic 4f-electron charge cloud relative to the electron orbitals of the nitrogen or the hydrogen atoms. At the R-ions with $\alpha_J < 0$ (Tb, Dy, Ho), the magnetic moment μ of the rare-earth ion is perpendicular, while at the R-ions with $\alpha_J > 0$ (Sm, Er) it is parallel [11] to the large axis of the 4f-electron charge cloud. This particularity of the R-ions electron structure explains why signs of the anisotropy constants R_1^R are in agreement with signs of the Stevens factor.

Fig. 3. Magnetostriction $(\lambda_{\parallel} - \lambda_{\perp})$ at 1.3 T, measured from powder-pressed samples of Tb_2Fe_{17} $(N, H)_x$. (a and b), $Dy_2Fe_{17}(N, H)_x$. (c).

Table 2
Stevens factors for different R elements entering into R_2Fe_{17} compounds and the sign of the first MCA constants of the rare-earth sublattice at hydrogenation $R_1^R(H)$ and nitrogenation $R_1^R(N)$

R	α_J*10^{-2}	$R_1^R(H)$	$R_1^R(N)$
Tb	− 1.01	(?)	+
Dy	− 0.63	−	+
Ho	− 0.22	−	+
Er	0.25	+	−

longitudinal magnetostriction differences cannot be accurately determined for Ho_2Fe_{17} because of the small value of the effect. However hydrogenation and nitrogenation induce a significant negative magnetostriction $(\lambda_{\parallel} - \lambda_{\perp}) = - (40–80) \times 10^{-6}$ in

Table 3
Stevens factors for different R elements entering into R_2Fe_{17} compounds and signs of the magnetostriction constants $(\lambda_{\parallel} - \lambda^{\perp})$ for R_2Fe_{17} $(N, H)_x$

R	α_J*10^{-2}	$x = 0$	Hydride	Nitride
Tb	− 1.01	+	−	−
Dy	− 0.63	+	−	−
Ho	− 0.22	?	−	−
Er	0.25	−	+	?

this compound. The data presented in Fig. 3 and in Table 3 show that the initial intermetallic compounds and synthesized interstitial compounds exhibit opposite signs of magnetostriction.

One can understand our results taking into account that the rare-earth ion of the initial compound is surrounded in the basal plane by six atoms of iron [2]. The 4f electron charge cloud rotates under the action of the magnetic field. This rotation results in the change of interatomic distances along the large axis of the 4f- electron cloud due to the change of the interaction between the 4f-electrons and ions of iron. The interstitial nitrogen atoms are accommodated in the octahedral positions [2], which are in the basal planes of the hexagonal cell amidst the hexagonal edges of Fe atoms. The hydrogen atoms are accommodated in tetrahedral positions [2]. The appearance of negative charges of H and N in these positions close to the 4f-electron cloud produces a repulsion and expansion of interatomic distances along their interaction line. Thus, the interstitial atoms essentially change the character of the interaction in the rotation of the 4f-electron cloud of the R-ions under the action of the magnetic field. This mechanism results in the experimentally discovered sign change of the magnetostriction constant on inserting the interstitial elements.

According to Refs. [5,15,16] for the easy plane materials with strong anisotropy, the values of $(\lambda_{\parallel} - \lambda_{\perp})$ measured in low fields on polycrystalline samples reflect the elliptical distortions of the basal planes, since contribution to the magnetostriction from the rotation of magnetization in the basal planes is most considerable. For R_2Fe_{17} compounds we suppose, that this situation takes place at fields up to 1.3 T at low temperatures.

Both magnetostriction and magnetic anisotropy depend on the values of the electric fields at the site of accommodation of the R-ions. The electric field gradient V_{zz} is characterized not only by the charges of ambient ions, but also by the effects related to the hybridization of 5p-electrons of R-ions with s- and p-electron states of interstitial atoms [17], the value of V_{zz} in R_2Fe_{17} compounds increases strongly for some interstitial atoms (C and N). As a result, one can assume a strong change of the parameters of both magnetocrystalline and magnetoelastic interaction. As shown by our results, the values and signs of these effects depend essentially on magnetic moment orientation of R-ions relative to the large axes of an aspherical distribution of the 4f-electrons charge density.

4. Conclusion

The results show that hydrogenation and nitrogenation lead to an opposite change of sign of the first MCA constants of the rare earth sublattice in $R_2Fe_{17}H_x$ and $R_2Fe_{17}N_x$. The direction of MCA value changes at hydrogenation and nitrogenation is consistent with the signs of the Stevens factors which describe the structure of the 4f-subshell of the R-ions. The change of the sign of magnetostriction found at hydrogenation and nitrogenation indicates, that the interstitial atoms have a significant effect on the magnetoelastic interaction of iron atoms and the anisotropic electron 4f-subshell of R ions.

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